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Organophosphate flame retardants in the indoor and outdoor dust and gas-phase of Alexandria, Egypt

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31 **Highlights**

- 32 • Indoor levels of OPFRs were significantly higher than outdoors.
- 33 • PBDEs>OPFRs> NFRs and OPFRs>PBDEs>NFRS In the gaseous and dust samples respectively.
- 34 • TDCIPP, TCIPP, TBOEP and TPHP dominated OPFRs in all samples with more indoor variability.
- 35 • Significant log-linear $K_{\text{dust-air}}-K_{\text{OA}}$ relationships indicated equilibrium partitioning.
- 36 • Dermal and ingestion pathways are important exposure routes.

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57 **Abstract**

58 Little is known about the presence of organophosphate flame retardants (OPFRs) as a substitute
59 for polybrominated diphenyl ethers in developing countries. This study investigated - for the first
60 time - concentrations, sources and exposure levels of OPFRs in the indoor and outdoor
61 environments of Alexandria, Egypt, in dust and gas-phase samples. Passive samplers were
62 deployed (n = 78) to determine gaseous concentrations, and various dust samples were collected
63 from apartments (n = 25), working places (n = 14), cars (n = 18), and outdoors (OD, n = 30). Indoor
64 concentrations (air: 7.0 – 64 pg/m³; dust: 150 – 1,850 ng/g) were significantly higher than outdoor
65 (2.0 – 16 pg/m³ and 83 – 475 ng/g) concentrations. Tris-1,3-dichloropropyl phosphate (TDCIPP),
66 tris(1-chloro-2-propyl) phosphate (TCIPP), tri (2-butoxyethyl) phosphate (TBOEP) and triphenyl
67 phosphate (TPHP) dominated in all samples with more indoor variabilities. Profiles of OPFRs in
68 OD and floor dust (collected from carpets and floors) were similar but differed from elevated fine
69 dust (collected 1 m above the floor from all available surfaces), possibly due to the influence of
70 carryover of OD by shoes. Despite the high uncertainty in dust – air partitioning coefficients,
71 significant log-linear relationships were observed with octanol – air-partitioning coefficients in all
72 microenvironments, indicating an equilibrium partitioning between dust and vapor. **Exposure**
73 **assessment indicated the importance of the dermal exposure route for adults and ingestion route**
74 **for children.**

75 **Keywords:** OPFRs, dust, gas-phase, indoor, outdoor, equilibrium partitioning, **exposure**

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79 **1. Introduction**

80 Halogenated organophosphate flame retardants (OPFRs) are now widely used in consumer
81 products (textiles, car upholstery, furniture, building materials, plastics and electronic equipment)
82 as a replacement for polybrominated diphenyl ethers (PBDEs) to reduce **flammability** (Larsson et
83 al., 2018; Van den Eede et al., 2011). Non-halogenated ones are also used as plasticizers and floor
84 polishes (Stapleton et al., 2009; van der Veen and de Boer, 2012). Because they are used as additive
85 flame retardants, OPFRs can undergo volatilization and/or dissolution and spread in the
86 environment (Kurt-Karakus et al., 2017). Accordingly, OPFRs have been detected in all
87 environmental compartments (Abdallah and Covaci, 2014; Cao et al., 2012, 2014; Dodson et al.,
88 2012; Salamova et al., 2014). They were also reported in biota (Sundkvist et al., 2010), human
89 blood and milk (Shah et al., 2006; Sundkvist et al., 2010) indicating their bioaccumulation
90 potential. Some OPFRs are known to have mutagenic and carcinogenic effects, alter human
91 thyroid hormone levels (TDCIPP, TCIPP and TPHP; Behl et al., 2016; Hendriks and Westerink,
92 2015; Noyes et al., 2015; Preston et al., 2017; Zhang et al., 2016), cause endocrine disruptive
93 effects (TPHP; Kojima et al., 2013), act as neurotoxins (TDCIPP; Yuan et al., 2016), and could
94 cause asthma and allergic rhinitis (TNBP; Araki et al., 2013). In the EU, some chlorinated OPFRs
95 are classified as either category 2 (tris-1,3-dichloropropyl phosphate) (Abdallah and Covaci, 2014)
96 or category 3 (tris-2-chloroethyl phosphate) (Abdallah and Covaci, 2014) carcinogens.

97
98 **Low density polyethylene sheets (LDPE) have been used for monitoring of atmospheric HOCs**
99 **(Bartkow et al., 2005, 2004; Kennedy et al., 2007; Khairy and Lohmann, 2018, 2017, 2014, 2013,**
100 **2012). Compared to other passive samplers, LDPE is the simplest (in its chemical makeup),**
101 **cheapest and easy to deploy (Lohmann, 2012). Extracts from LDPE seldomly need any of the**
102 **complicated cleanup techniques. LDPE can be operated in the uptake (kinetic) or equilibrium**

103 (thermodynamic) sampling mode by varying the thickness of the PE and the exposure time (days,
104 weeks and months), and was previously calibrated/validated for measuring vapor phase
105 concentrations of HOCs (Khairy and Lohmann, 2014).

106
107 Although OPFRs have been detected in the dust from various indoor microenvironments of North
108 America (Cao et al., 2014; Dodson et al., 2012; Schreder and La Guardia, 2014; Shoeib et al.,
109 2012; Stubbings et al., 2018), Asia (Ali et al., 2013; Cao et al., 2012; Kanazawa et al., 2010) and
110 Europe (Brommer et al., 2012; Cao et al., 2014; Fromme et al., 2014; Kademoglou et al., 2017;
111 Kanazawa et al., 2010), few studies were performed in Africa (Abdallah and Covaci, 2014; Shoeib
112 et al., 2019). Additionally, studies investigating the levels of OPFRs in the indoor air (Cequier et
113 al., 2014) and outdoor dust and air are very rare (Cequier et al., 2014; Möller et al., 2011; Salamova
114 et al., 2014). Previous indoor studies collected floor dust (FD), and one study investigated and
115 compared the levels of chlorinated OPFRs in FD and elevated fine dust (EFD), which is collected
116 ~ 1 meter above the ground (Allgood et al., 2017). In previous studies, some variations were
117 observed in the levels and patterns of PBDEs and other flame retardants between FD and EFD (Al-
118 Omran and Harrad, 2016; Allgood et al., 2017; Björklund et al., 2012; Cequier et al., 2014; Khairy
119 and Lohmann, 2018).

120 In a recent study (Khairy and Lohmann, 2018), we investigated the presence of PBDEs and
121 alternative flame retardants (NFRs) in Alexandria, Egypt and found significantly higher
122 concentrations ($p < 0.05$) of PBDEs and NFRs in the gaseous and EFD samples of the indoor
123 microenvironments compared to the outdoor environment. In the current study, we report on
124 concentrations of OPFRs for that sample set. For the vapor-phase samples, low density
125 polyethylene passive samplers (LDPE) were used, which has proven to be an easy, cost-effective
126 monitoring tool for hydrophobic organic compounds (HOC) in the ambient air (Bartkow et al.,

127 2004; Booij et al., 2002; Khairy and Lohmann, 2014; McDonough et al., 2016) but rarely used
128 indoors (Khairy and Lohmann, 2018). LDPE sheets were deployed at different outdoor locations
129 (n = 30) and various indoor microenvironments (n = 30), including cars (n = 18). EFD samples
130 were collected from the same locations as LDPE. At the same time, FD was collected from selected
131 homes (n = 9). Our main objectives were to: i) investigate and compare concentrations, profiles
132 and potential sources of OPFRs in the indoor and outdoor environments, ii) determine variations
133 in the concentrations and profiles of OPFRs in EFD and FD, and iii) compare the concentrations
134 and gas-particle distribution of OPFRs with the legacy flame retardants (PBDEs and NFRs) and
135 iv) estimate human exposure to OPFRs via inhalation, ingestion and dermal contact for toddlers,
136 children and adults. To our knowledge, this is the first comprehensive study to measure OPFRs in
137 the indoor and outdoor environments, and to utilize LDPE as an indoor passive sampler for OPFRs.

138

139 **2. Materials and Methods**

140 Detailed description of the study area, sampling, extraction and cleanup, instrumental analysis,
141 selected physicochemical properties, calculation of atmospheric concentrations from LDPE and
142 the estimation of the daily intakes of OPFRs are provided in Appendix A (supplementary
143 information), in Khairy and Lohmann, 2018 and are briefly summarized below.

144

145 Indoor and outdoor samples were collected from Alexandria, Egypt (Fig. A1) during the late
146 autumn – winter of 2014 (November – December) when indoor ventilation (**indoor-outdoor air**
147 **exchange**) effects are minimum. EFD (settled dust from elevated surfaces such as tables, shelves
148 and bookcases; Al-Omran and Harrad, 2016) was collected 1 m above the floor from the living
149 (working) areas in apartments (n = 16) and working places (n = 14) using an Electrolux JetMaxx
150 Bag Canister Vacuum cleaner (Model EL4042A) in cellulose thimbles fitted between the crevice

151 tool and the vacuum tube. FD was collected from selected homes (n = 9) by slowly passing the
152 crevice tool of the vacuum cleaner on carpets and bare floor of the living area. The dust was
153 allowed to pass to the dust collection bag (Kajiwara and Takigami, 2016). Samples were wrapped
154 in a pre-combusted aluminum foil, sealed in plastic zip bag, and stored at -20 °C until analysis.
155 For cars, dust (n = 18) was collected from all the available surfaces except the floor. Participants
156 were asked to follow specific guidelines for the samples to be valid (see Appendix A and Table
157 A1 for more details).

158
159 Outdoor dust samples (n = 30) from the same locations as the indoor samples, were collected from
160 smooth surfaces using small plastic brushes and a small aluminum shovel. Samples were kept in
161 small amber glass jars and stored in a freezer at -20 °C until analysis.

162 LDPE [10 × 30 cm strip of ~2 g each (51 μm thickness) for the outdoor samples, and 10 × 20 cm
163 strip of ~1 g each (25 μm thickness) for the indoor samples] were pre-cleaned and spiked with
164 performance reference compounds (PRCs) (Booij et al., 2002). Outdoor samples (n = 30 x
165 duplicates) were deployed for 2 months near the indoor sampling locations in two inverted bowls
166 as a shelter for protection against sunlight and precipitation. In the indoor microenvironments, one
167 LDPE sheet was deployed for 2 months at each of the sampled rooms (n = 2 – 3) of the living area
168 starting two weeks before the dust sampling campaign. Samplers were hung in protected places
169 away from direct exposure to the light and direct contact with participants. The total number of
170 deployed LDPE were 66 (33 x duplicates) at apartments, 36 at the cars, and 60 at working places
171 (total = 162 samples). In the extraction/analysis step, all LDPE sheets deployed within a unit
172 (apartment or working place) were pooled and extracted as one sample (n = 16, 14 and 18 x
173 duplicate for apartments, working places and cars respectively).

174

175 Dust samples (indoor and outdoor) were sieved through a 3-inch, 100 mesh (150 μm) stainless
176 steel sieve (Dodson et al., 2012), and ~ 0.50 g dry weight were extracted in an ultrasound after
177 spiking with labelled OPFR surrogates. Samples were then purified and fractionated (F1 and F2)
178 over silica gel. F2 containing the OPFRs was concentrated to a final volume of ~ 25 μL (in
179 methylene chloride) after the addition of the injection standard (p-terphenyl- d_{14}). LDPE samplers
180 were spiked with surrogate standards (same as above) and extracted twice for 24 h each. After
181 extraction, no further cleanup was required and the extracts were concentrated as shown above for
182 the dust samples.

183 Samples were analyzed for 12 OPFRs [tris-2-chloroethyl phosphate (TCEP), tris(1-chloro-2-
184 propyl) phosphate (TCIPP), tris-1,3-dichloropropyl phosphate (TDCIPP), tris(2,3-dibromopropyl)
185 phosphate (TDBPP), tri-n-butyl phosphate (TNBP), tri (2-butoxyethyl) phosphate (TBOEP), 2-
186 ethylhexyldiphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP), triphenyl
187 phosphate (TPHP), tri-o-totyl phosphate (o-TMPP), tri-m-totyl phosphate (m-TMPP) and tri-P-
188 totyl phosphate (p-TMPP)] on an Agilent 6890N gas chromatograph coupled to a Waters Quattro
189 Micro mass spectrometer (GCMS/ MS) in electron ionization mode (EI, 70 eV) using multiple
190 reaction monitoring (MRM).

191
192 Field blanks, matrix spikes, and duplicate samples (30% of the total dust samples and all the LDPE
193 samples) were included with each sample batch. Field blanks (10 for dust and 10 for LDPE) were
194 analyzed with the samples (Table A2), and samples were corrected for the blanks. When an analyte
195 was not detected, the noise was quantitated for the limit of detection (LOD) calculations. LODs
196 were determined in the different matrices as the upper limit of the 95% confidence interval for the
197 field blanks (Table A3). We used $\frac{1}{2}$ the LOD for concentrations that were below the detection
198 limit. Recoveries of the surrogate standards generally ranged from 68 – 90 % and 66 – 94 % for

199 the outdoor and indoor LDPE respectively, 60 – 85 % for the outdoor dust, 61 – 90 % for the
200 indoor fine dust and 62 – 94 % for the floor dust. Matrix spikes recoveries (n = 6 for LDPEs and
201 7 for dust) ranged from 74 ± 3.0 % (TNBP) to 101 ± 1.0 % (m-TMPP) for the LDPE and from 73
202 ± 3.0 % (TNBP) to 104 ± 1.0 % (TPHP) for the dust (Table A4) with a relative standard deviation
203 $< 20\%$. Results of the replicate analysis of LDPE and the dust samples indicated that the
204 reproducibility of the analysis ranged from 18 % – 25 %.

205 For **exposure assessment**, the daily exposure doses from inhalation, ingestion and dermal exposure
206 pathways were calculated according to the USEPA guidelines (Means, 1989) as detailed in Khairy
207 and Lohmann, 2018 and as shown in Appendix A.

208
209 Analysis of variance (ANOVA) and the student t-test were performed with SigmaPlot 11. All
210 numbers were log-transformed before the statistical test for normality. Factor analysis (FA) and
211 bivariate correlation were performed with IBM SPSS (V 23, USA). In the factor analysis model,
212 principle component analysis (PCA) was used as the extraction method with Kaiser Normalization
213 and varimax rotation. Only factors with eigen values > 1 were used for identification of the possible
214 sources. Before applying FA, all numbers were log transformed for normality. Each sample was
215 entered as a separate variable, and each sample included concentrations of PBDEs and NFRs from
216 our previous work (Khairy and Lohmann, 2018) and OPFRs from the current study. Independent-
217 samples t-test and Repeated Measures of ANOVA were used to determine the difference in OPFR
218 levels between the different samples and the indoor microenvironments. Correlation analyses were
219 used to investigate the possible sources of OPFRs.

220

221 **3. Results and Discussion**

222 *3.1. Indoor Concentrations*

223 3.1.1. Vapor Phase Samples

224 Concentrations of \sum OPFRs in the gas phase ranged from 6.0 - 39 pg/m³ (apartments), 7.0 - 64
225 pg/m³ (working places) and 10 - 45 pg/m³ in cars (Table A5). Cars showed the highest median
226 concentration (20 pg/m³) followed by working places (18 pg/m³) and apartments (15 pg/m³). TPHP
227 was detected in 100 % of the samples with comparable median concentrations in cars (2.5 pg/m³)
228 and working places (2.3 pg/m³), and a lower median concentration in apartments (0.79 pg/m³).
229 TDCIPP was detected in all the samples from apartments (median: 3.0 pg/m³) and cars (1.1 pg/m³),
230 TBOEP in all the samples from working places (median: 1.2 pg/m³), and TCIPP in all the car
231 samples (median: 7.2 pg/m³; Table A5). TCEP, TBOEP and EHDPP were below the LOD in all
232 the samples from apartments and working places, whereas only EHDPP was below LOD in cars.
233 TCEP and TBOEP were detected in 61 % (median: 1.8 pg/m³) and 89 % (median: 1.3 pg/m³)
234 respectively of the car samples.

235
236 For each indoor microenvironment, there was a different profile of OPFR observed (Fig. A2).
237 Apartments were generally dominated by the chlorinated organophosphate flame retardants
238 (mostly TCIPP and TDCIPP, less so of TNBP and TPHP, see Fig. A2a). This variability in the
239 contributions was also observed in working places (58 % with TCIPP, 21 % with TNBP and 14 %
240 with TDCIPP; Fig. A2b) and cars (67 % of the samples with TCIPP and 28 % with TDCIPP; Fig.
241 A2c). In cars, TDCIPP was more abundant in German-made cars compared to TCIPP in Japanese
242 and Korean cars. The varying contributions of OPFRs imply that volatility alone cannot explain
243 these observed OPFR profiles in the different microenvironments and that probably the type of
244 OPFR used in furniture, car upholstery, plastics, among others, is the main reason for this observed
245 variability.

246

247 3.1.2. Dust Samples

248 Σ OPFRs ranged from 153 to 1,117 ng/g, 189 – 1,138 ng/g, and 272 – 1,849 ng/g in the EFD of
249 the apartments, working places and cars respectively. Concentrations of OPFRs in the cars
250 (median: 692 ng/g) were significantly higher (one-way repeated measures of ANOVA; $p < 0.001$)
251 than concentrations observed at working places (median: 359 ng/g) and the apartments (Table A6)
252 which was similar to what was previously found in Cairo, Egypt (Abdallah and Covaci, 2014) and
253 Germany (Brommer et al., 2012).

254
255 Concentrations of Σ OPFRs in the FD samples of the apartments ranged from 122 ng/g to 514 ng
256 with a median concentration of 243 ng/g (Table A6). No statistically significant difference was
257 observed between detected samples in the FD and the EFD (162 – 1,117 ng/g; median: 260 ng/g).

258
259 Some variability was observed when the different microenvironments were compared with respect
260 to the detected analytes (Fig. 1b). TDCIPP was detected in all the EFD samples (Table A6). TPHP
261 was also detected in 100 % of the apartment, working places, FD and in 94 % of the car samples
262 ($n = 18$). TBOEP and TCIPP were detected in all the EFD samples from working places and cars
263 respectively. (Table A6). TNBP was below LOD at apartments and working places but detected
264 in 56 % of the car samples. TDBPP, TEHP, EHDPP and o-, m- and p-TMPP were the least
265 abundant and have low detection frequencies in all the samples. Our results were in good
266 agreement with other studies (either EFD or FD) in Cairo, Egypt (Abdallah and Covaci, 2014),
267 Norway (Cequier et al., 2014), Japan (Kanazawa et al., 2010) and USA (Dodson et al., 2012;
268 Stapleton et al., 2009).

269
270 TDCPP dominated in 75 % and 38 % of the indoor samples of the apartments and working places
271 respectively (Fig. A3a, b) followed by TPHP (13 % and 19 % respectively) and TCIPP (6.0 % and

272 13 %) and TBOEP (6.0 % and 13 %). In cars (Fig. A3c), TCIPP dominated OPFR profiles in 61
273 % of the samples (mainly Japanese and Korean cars) followed by TDCIPP (in the German cars;
274 28 %), TBOEP (13 %) and TPHP (only in one sample). TDCIPP was the dominant analyte in dust
275 samples collected from cars in Germany (Brommer et al., 2012). TCIPP and TPHP were also found
276 to be the dominant analytes in cars from Kuwait (Ali et al., 2013) and Pakistan (Ali et al., 2013)
277 respectively.

278
279 Unlike the EFD, FD samples of the apartments were dominated by TBOEP (59 ng/g) comprising
280 11 – 36 % of the total concentrations followed by TPHP (36 ng/g; 11 - 22 %) and TDCIPP (35
281 ng/g; 5.0 - 25 %), which was in good agreement with other studies worldwide (Brommer et al.,
282 2012; Cequier et al., 2014; Dodson et al., 2012; Kanazawa et al., 2010; Shoeib et al., 2019).
283 TBOEP is used in floor polishing (waxing) (Dodson et al., 2012) and thus its predominance in the
284 FD samples is not surprising. However, the difference in the observed profiles between the EFD
285 and the FD of the same sampling locations (Fig. A3a, d) may possibly indicate different sources
286 (see below). In the apartments sampled for EFD and FD (n = 9), median concentrations of TCEP
287 (14 ng/g), TCIPP (29 ng/g) and TDCIPP (70 ng/g) in the EFD samples were higher than in the FD
288 samples (<LOD, 18 ng/g and 35 ng/g respectively) but statistically insignificant. Similar finding
289 was observed for TDCIPP and TCIPP in EFD and FD samples collected from a university campus
290 in California, USA (Allgood et al., 2017). In contrast, median concentrations of TBOEP (58 ng/g)
291 and TPHP (47 ng/g) in the FD samples of the current study were higher than concentrations
292 reported for the EFD samples (26 and 30 ng/g respectively).

293 294 **3.2. Outdoor Concentrations:**

295 *3.2.1. Vapor Phase Samples*

296 Outdoor vapor phase concentrations of Σ OPFRs ranged from 2.4 to 9.0 pg/m^3 and 2.3 to 16 pg/m^3
297 at the residential-industrial and residential sites respectively (Table A5) with no statistical
298 significance difference in the detected concentrations (t-test, $p > 0.05$). TNBP showed the highest
299 median concentration at the residential - industrial (1.9 pg/m^3) and residential sites (2.0 pg/m^3)
300 and was detected in 67 % and 73 % respectively of the samples ($n = 15$ each) probably due its
301 higher volatility compared to the other OPFRs (Reemtsma et al., 2008). TCIPP was the second
302 highest at the residential site (1.9 pg/m^3) but it was only detected in 47 % of the samples (Table
303 A5). All the other OPFRs displayed lower median concentrations ($< 0.70 \text{pg}/\text{m}^3$). TDBPP, TEHP,
304 o-TMPP, m-TMPP and p-TMPP were below LOD in all the samples. Except for TCIPP, which
305 showed significantly higher concentrations (t-test, $p < 0.05$) at the residential sites (2.0 pg/m^3
306 compared to 0.90 at the residential-industrial sites), no statistical significance difference was
307 observed between the residential and residential- industrial sites for all the other detected OPFRs
308 (Fig. 1b).

309
310 TNBP and TCIPP dominated in the outdoor samples (Fig. A2d, e) comprising 3.0 – 92 % and 10
311 – 53 %, respectively, of the total concentrations of OPFRs.

312 313 3.2.2. Dust Samples

314 Concentrations of Σ OPFRs generally ranged from 83 – 480 ng/g with comparable concentrations
315 at the residential and residential – industrial regions (Table A6). Median concentrations of TCEP,
316 TDBPP, TEHP, EHDPP, o-TMPP and p-TMPP were below LOD at all the sites, whereas median
317 concentrations of TNBP were below LOD only at the residential sites (Table A6). Some variability
318 was observed in the contributions of the investigated OPFRs in the outdoor samples (Fig. A3e, f).
319 At the residential sites, TPHP showed the highest median concentration (32 ng/g) comprising 3.0

320 - 49 % of the total concentrations followed by TDCIPP (median: 28 ng/g; % contribution: 3.0 - 59
321 %), TCIPP (20 ng/g; 3.0 - 30 %) and TBOEP (18 ng/g; 1.0 – 28 %). At the residential – industrial
322 sites, the following descending order was observed: TBOEP (30 ng/g; 16 - 51 %) > TPHP (22
323 ng/g; 12 - 69 % each) > TNBP (16 ng/g; 11 – 33 %) > TDCIPP (15 ng/g; 11 - 33 %).

324

325 **3.3. Comparison with Other Studies Worldwide**

326 As shown in Fig. 2 and Table A7, detected vapor phase concentrations in all the indoor
327 microenvironments were much lower than those reported for Norwegian houses (Cequier et al.,
328 2014) (Fig. 2a), the North Sea (Möller et al., 2011) and the Great Lakes (Salamova et al., 2014)
329 (Table A7). Similarly, detected **dust** concentrations of OPFRs in the current study were generally
330 lower than worldwide concentrations observed in the indoor microenvironments (Ali et al., 2013,
331 2012; Brommer et al., 2012; Cequier et al., 2014; Dodson et al., 2012; Kademoglou et al., 2017;
332 Kanazawa et al., 2010; Van den Eede et al., 2011) (Fig. 2), but comparable to previously reported
333 concentrations for the FD samples in Cairo (**sampled during 2012 – 2013**), Egypt **in one study**
334 (**Abdallah and Covaci, 2014**) **and much lower than reported concentrations of OPFRs in FD**
335 **samples collected from Cairo (sampled during 2013 – 2014) in another study (Shoeib et al., 2019).**
336 It is important to mention that differences in sampling year, sample type (EFD vs FD) and the
337 general characteristics of the microenvironments (year of construction, number of foamed
338 furniture and number of electronics) are all major variables that could greatly influence the validity
339 of such comparison.

340

341 **3.4. Comparison between levels and profiles of OPFRs in the different microenvironments**

342 **3.4.1. Vapor phase**

343 Chlorinated organophosphate flame retardants dominated all the samples from the investigated
344 indoor microenvironments, and comprised 46 – 69 % of the total vapor phase concentrations.
345 TCIPP concentrations were significantly higher (One-Way repeated measures of ANOVA, $p <$
346 0.01) in cars (median 7.2 pg/m^3) compared to working places (median: 2.9 pg/m^3) and apartments
347 (median: 4.0 pg/m^3) In contrast, TDCIPP showed significantly lower concentrations ($p < 0.008$)
348 in cars (median: 1.1 pg/m^3) compared to apartments and working places (median: 3.0 and 2.6
349 pg/m^3 respectively; Fig. 1a), and TBOEP and TPHP concentrations were significantly higher ($p <$
350 0.01) at cars and working places compared to apartments (Fig. 1a). No statistically significant
351 differences were observed for concentrations of TCEP, TNBP and EHDPP in the different indoor
352 microenvironments.

353 354 *3.4.2. Elevated fine dust*

355
356 Detected EFD concentrations of OPFRs at the apartments were lower than concentrations reported
357 for the working places and cars (Fig. 1c). TBOEP and TPHP concentrations at working places
358 were significantly higher (Repeated measures of ANOVA, $p: 0.024, 0.01$) than detected
359 concentrations at the apartments. Similarly, TCEP was detected at working places (median: 17
360 ng/g), but below LOD at the apartments. TBOEB and TPHP were the dominant OPFRs in the FD
361 collected from working places in Belgium (Van den Eede et al., 2011) and Germany (Brommer et
362 al., 2012). We assume that the higher contribution of the chlorinated OPFRs is attributed to their
363 wide use as flame retardants in PUFs and as plasticizers (Larsson et al., 2018; Stapleton et al.,
364 2009). It has been suggested that chlorinated alkyl OPFRs are now used as a replacement for the
365 penta-BDE formulation in polyurethane foam (PUFs) (Dodson et al., 2012). As was previously
366 observed in California (Dodson et al., 2012), TDCIPP and TCIPP were not correlated with detected

367 concentrations of TCEP ($r = 0.23, 0.33, p = 0.067 - 0.089$) as both can be used as a replacement
368 for the TCEP. Additionally TDCIPP is known to be an expensive flame retardant and is used only
369 when an efficient flame retardant is needed (Dodson et al., 2012) which explains its wide use in
370 apartment foam goods. Our findings for the indoor microenvironments were similar to results from
371 Cairo, Egypt (dominance of TDCIPP and TPHP) and in US household dust (Stapleton et al., 2009)
372 but different from Norway (Cequier et al., 2014), California, USA (Dodson et al., 2012), Japan
373 (Kanazawa et al., 2010) and FD samples from houses in Cairo, Egypt (Shoeib et al., 2019), where
374 TBOEP (164 – 87,200 ng/g) showed the highest median concentration in either the FD or EFD.

375
376 In cars, dust samples were dominated by TCIPP (median: 184 ng/g), TBOEP (median: 154 ng/g),
377 TPHP and TDCIPP (90 ng/g each), which is in good agreement with dust samples collected from
378 cars in Cairo, Egypt (Abdallah and Covaci, 2014) and Kuwait (Ali et al., 2013). In cars,
379 concentrations of TCIPP and TBOEP were significantly higher (Repeated measures of ANOVA,
380 $p < 0.008$) than apartments and working places. Similarly, TPHP concentrations in cars were
381 significantly higher ($p = 0.01$) than apartments. Chlorinated OPFRs are used as plasticizers in car
382 interior and as flame retardants in upholstery foam (Van den Eede et al., 2011; van der Veen and
383 de Boer, 2012), which may explain their higher detected concentrations in cars. TBOEP is also
384 used in rubber and in plastics (Van den Eede et al., 2011; van der Veen and de Boer, 2012), and
385 TPHP as a flame retardant, plasticizer, synthetic rubber and thermoplastics (Abdallah and Covaci,
386 2014).

387 388 **3.5. OPFRs vs PBDEs and NFRs**

389 Detected OPFR concentrations were compared with concentrations of PBDEs and NFRs measured
390 in the same samples (Khairy and Lohmann, 2018). Vapor phase concentrations of PBDEs (Fig.

391 3a) were significantly higher (one-way repeated measures of ANOVA; $p < 0.001$) than
392 concentrations of NFRs and OPFRs. On the other hand, concentrations of OPFRs in the dust
393 samples (Fig. 3b) were the highest (one-way repeated measures of ANOVA; $p < 0.001$), followed
394 by PBDEs and NFRs which showed the lowest concentrations. This is probably a reflection of the
395 increased dependence on OPFRs in consumer goods in recent years. Detected concentrations of
396 NFRs in the samples imply that they have not been widely used in the imported consumer products
397 in Egypt. Interestingly, gaseous concentrations of PBDEs were higher than OPFRs. This could be
398 attributed to the higher detected gaseous concentrations of the lower brominated PBDEs (BDE- 2,
399 8, 15, 28) (Chaoyang Yue and Loretta Y. Li, 2013) in addition to BDE-47 and 99, which have
400 higher vapor pressure [more volatility; $\log P_L$ (Pa) = -0.67 to -2.9] (Brommer et al., 2014) than
401 the dominant OPFRs [$\log P_L$ (Pa) = -1.3 to -4.3], and the longer usage history of PBDEs.

402 403 **3.6. Indoor vs Outdoor OPFRs**

404 All the gaseous and EFD concentrations in the indoor samples (excluding cars) were significantly
405 higher (t-test, $p < 0.006$) than their corresponding outdoor samples. Additionally, variability in the
406 observed profiles (Fig. A2, A3) in the indoor and outdoor environments suggests that detected
407 concentrations in the indoor microenvironments are mainly from the indoor emission sources and
408 that the indoor microenvironments are acting as a source of OPFRs to the outdoor environment
409 (Indoor/outdoor > 1 for all analytes).

410
411 Some variations in the detected OPFRs were observed between the EFD and FD samples
412 (dominance of the chlorinated FRs in the EFD compared to TBOEP and TPHP in FD) as outlined
413 in Fig. A4. Similar to FD, median concentrations of TPHP and TBOEP in the outdoor dust were

414 higher than TDCIPP. This implies that OPFRs in EFD and FD samples for the same locations were
415 probably produced and/or influenced by different sources.

416 For further investigation, factor analysis (FA) was performed separately for the vapor phase and
417 dust samples. In this analysis, OPFR data from the current study and NFR and PBDE data from
418 our previous study were included. Samples were entered as the variables. The main purpose was
419 to check the variabilities/similarities between the different microenvironments, the different dust
420 samples investigated (EFD vs FD vs OD) and within each microenvironment. Results are shown
421 in Tables A8 and A9. For the vapor phase, four factors were extracted identifying 91 % of the
422 variance. Factor 1 was responsible for 31 % of the total variance and was heavily loaded on the
423 outdoor samples and moderately loaded on the majority of the samples of the indoor
424 microenvironments (Table A8) thus representing the outdoor environment. Factor 2 identified 29
425 % of the variance and was heavily loaded on the indoor samples from working places and cars,
426 few outdoor samples, and moderately loaded on the majority of the outdoor samples. Factor 3
427 identified 21 % of the total variance and was heavily loaded on the indoor samples. Factor 4
428 identified 10 % of the total variance and was heavily loaded on one indoor sample from apartments
429 and low to moderately loaded on the rest of the samples. The output of the FA for the gaseous
430 samples separated the outdoor samples from the indoor samples, which were loaded on several
431 factors. This is a reflection of the between (indoor vs outdoor and between the different indoor
432 microenvironments) and within (investigated samples within a given indoor microenvironment)
433 variabilities in the profiles of flame retardants.

434
435 Similar outputs (due to variations in the profiles of flame retardants) were observed for the dust
436 samples (Table A9), where EFD samples from the different indoor microenvironments were
437 loaded on two factors (Factors 1 and 3) and were separated from the outdoor dust samples (Factor

438 2), which were loaded together with the FD samples. The loading of FD and outdoor dust on the
439 same factor is a reflection to the similarities in their profiles of OPFRs (Fig. A4), PBDEs and NFRs
440 (Khairy and Lohmann, 2018). Since all the samples were sieved (excluding the influence of
441 particle size differences in samples), we suggest that FD samples are probably affected by
442 carryover of dust by the shoes from the outdoor places. Based on our pre-sampling conditions (as
443 requested from volunteers as shown in the supplementary information), we assume that this
444 carryover process is of minimum influence on EFD samples.

445 446 **3.7. Sources and Relations between OPFRs in the Samples**

447 In the air and EFD samples (Tables A10, A11), significant correlations were observed between the
448 individual OPFRs (TCIPP, TCEP, TDCIPP, TPHP and TBOEP; $r = 0.45 - 0.62$, $p < 0.05$)
449 indicating possible common sources. TCIPP, TDCIPP and TBOEP were significantly correlated
450 with the number of foamed furniture in the air ($r = 0.39 - 0.54$, $p < 0.05$) and EFD samples ($r =$
451 $0.38 - 0.45$, $p < 0.05$), possibly due to the use of these OPFRs in foam-containing furniture (Van
452 den Eede et al., 2011; van der Veen and de Boer, 2012). TBOEP significantly correlated with the
453 type of floor in air and EFD, where concentrations increased in places with wood floors probably
454 due to its wide use as a floor polish (Dodson et al., 2012).

455
456 In cars, TCIPP in the vapor phase and dust samples ($r = 0.50, 0.67$; $p = 0.036, 0.002$) showed
457 significant positive correlation with the model year ($r = 0.52 - 0.67$, $p < 0.05$). TBOEP and
458 TDCIPP were significantly higher in the German cars ($r = 0.67 - 0.85$, $p < 0.05$) in both air and
459 dust samples (Tables A13, A14). However, these findings should be carefully considered due to
460 the small number of investigated samples ($n = 6$ each).

461

462 Based on the correlation analysis, other variabilities within the sampled indoor locations, origin
463 and age of the imported consumer goods greatly influenced the observed patterns and
464 concentrations of OPFRs in the indoor samples despite the observed significant correlations for
465 the chlorinated flame-retardants and TBOEP in the indoor microenvironments, which identified
466 their sources. Accordingly, a clear image about the possible sources of all the investigated OPFRs
467 could not be obtained in the current study as was previously observed for various organic flame
468 retardants in the indoor microenvironments of Norway (Cequier et al., 2014).

469 470 **3.8. Relationship between OPFRs in Air and Dust**

471 Equilibrium partitioning of OPFRs in air and dust of the same indoor and outdoor sampling sites
472 was investigated in the current study. Significant positive correlations between gaseous and dust
473 OPFRs (TCIPP, TDCIPP, TBOEP, TPHP, \sum OPFRs) were observed in the indoor
474 microenvironments ($r = 0.50 - 0.75$; $p < 0.006$) and cars ($r = 0.51 - 0.90$, $p < 0.01$), but only for
475 TDCIPP and \sum OPFRs in the outdoor environment ($r = 0.40 - 0.55$, $p < 0.03$). Similar findings were
476 observed for indoor OPFRs in Norway (Cequier et al., 2014), for PBDEs in Toronto, Canada
477 (Zhang et al., 2011) and for PBDEs and NFRs at Alexandria, Egypt (Khairy and Lohmann, 2018)
478 despite differences in sampling techniques (conventional air sampling in Norway vs PUF passive
479 samplers in Canada vs LDPE in Alexandria, Egypt). Log dust – air partitioning coefficients ($K_{\text{EFD-air}}$,
480 m^3/g) were calculated by **dividing** the detected concentrations in the dust samples by those
481 obtained from the LDPE. When these were plotted against log octanol – air partitioning
482 coefficients ($\log K_{\text{OA}}$), significant log-linear relationships were observed for the indoor
483 (apartments + working places, Fig. 4a), cars (Fig. 4b) and the outdoor environment (Fig. 4c)
484 indicating an equilibrium partitioning between air and the organic phase of the dust particles
485 (Weschler and Nazaroff, 2010). A similar finding was observed for FD samples. Equilibrium

486 partitioning between air and dust for a wide range of flame retardants was also previously observed
487 in Norway (Cequier et al., 2014). In contrast, significant log linear $K_{\text{dust-air}} - K_{\text{OA}}$ relationships were
488 only for PBDEs with $\log K_{\text{OA}} < 11$ and no relation for higher brominated ones in Toronto, Canada
489 (Zhang et al., 2011). In the current study, we observed strong log-linear correlations for all flame
490 retardants (Fig. 4). We assume that the difference in the passive samplers used is the reason for
491 this variation. In the study performed in Toronto, PUF samplers were used, which are known to
492 collect the vapor phase in addition to particles (Strandberg et al., 2018; Zhang et al., 2011) thus
493 overestimating vapor phase concentrations. In contrast, LDPE passive samplers have the
494 advantage of sampling gaseous phase with no influence from particles, thus assumed to give more
495 accurate estimation of the vapor phase concentrations.

496 Interestingly, $K_{\text{EFD-air}}$ values varied widely for the different flame retardants with the same K_{OA}
497 values. In general, $K_{\text{EFD-air}}$ values for OPFRs, were always higher (Fig. 4) than values calculated
498 for NFRs and PBDEs that showed comparable values. $K_{\text{EFD-air}}$ of TCEP (4.1) was double that of
499 BDE-2 (2.3) despite their close K_{OA} values (7.6 and 7.2 respectively). For flame retardants with
500 K_{OA} values ~ 10.5 , $K_{\text{EFD-air}}$ values of TDCIPP (4.5) and TPHP (4.5) were higher than calculated
501 values for hexabromobenzene (2.1) and BDE-47 (2.8). Three reasons could be responsible for this
502 observed trend: i) chemical differences (apolar bromines in PBDEs and NFRs vs monopolar
503 phosphate group in OPFRs); (ii) uncertainties in the physicochemical parameters (K_{OA}) and $K_{\text{PE-a}}$
504 and (iii) uncertainties in measured gaseous concentrations since underestimated gaseous
505 concentrations result in higher $K_{\text{EFD-air}}$ as was observed for OPFRs. In the current study, gaseous
506 concentrations of all flame retardants were determined using LDPE. Accumulated amounts of
507 flame retardants in the plastic sheets (C_{PE}) were converted to gaseous concentrations using LDPE-
508 air partitioning coefficients ($K_{\text{PE-A}}$, L/kg). $K_{\text{PE-A}}$ s for all the analytes were calculated from the

509 subcooled liquid vapor pressures (P_L , Pa) of the target analytes as shown elsewhere (Khairy and
510 Lohmann, 2014). However, several P_L values exist in literature with great variability. To study,
511 the influence of uncertainties in P_L , we used different available P_L values from literature to
512 calculate K_{PE-A} values, estimate gaseous concentrations and use these estimated concentrations to
513 calculate $K_{EFD-air}$ for the analytes. For PBDEs, we used the K_{PE-A} values from our field calibration
514 study (Khairy and Lohmann, 2014) and incorporated the estimated uncertainty for each congener.
515 P_L values for NFRs and OPFRs were obtained from SPARC calculator (Ruan et al., 2009), EPI
516 suite and Absolv (Ruan et al., 2009), in addition to literature (Bergman et al., 2012 and Dirtu et
517 al., 2013 for NFRs and Brommer et al., 2014 for OPFRs). As shown in Fig. 4, calculated $K_{EFD-air}$
518 values for all the analytes were within the uncertainty range (dashed red lines) estimated from the
519 uncertainties in P_L values. However, the highest $K_{EFD-air}$ uncertainties were observed for OPFRs
520 (39 – 200 %, average: 135 %) which were significantly higher (One Way Repeated Measures
521 ANOVA, $p < 0.001$) than $K_{EFD-air}$ uncertainties for NFRs (0.24 – 66 %) and PBDEs (20 – 75 %).
522 Future work should confirm that OPFRs partitioning to LDPE is as expected based on apolar
523 compounds.

524 **3.9. Human Exposure Assessment**

526 In the current study, the exposure to OPFRs via ingestion of EFD, inhalation (gaseous
527 concentrations) and dermal contact (with EFD) was investigated. The detailed description of the
528 models used and constants used are given in the supplementary information. For each exposure
529 route, daily exposure dose was calculated for adult males and females (both working and **non-**
530 **working**), children (> 6 years old) and toddlers. The exposure times (ET) at home, work, **cars**,
531 school and outdoor were obtained from the answers of the participants in the questionnaires. All
532 the other parameters such as body weight, inhalation rates, ingestion rates, dermal adherence rate,

533 surface area and absorbed dose were obtained from the EPA guidelines for human health risk
534 assessment (Means, 1989). **Calculated** daily dose for each target analyte from each exposure route
535 is given in Table A15. Total daily doses (sum of doses from inhalation + ingestion +dermal
536 contact) ranged from 0.050 – 1.2, 0.060 – 1.3, 0.050 – 1.2, 0.28 – 7.1 and 0.52 – 12 ng/kg bw/d
537 for adult **working** females, **non-working females**, adult males, children and toddlers respectively.
538 All daily doses of TCEP, TCIPP, TDCIPP, TNBP, TBOEP and TPHP from the ingestion pathway
539 (both worse- and best-case scenarios) were much lower than their corresponding oral reference
540 doses. For all the exposure routes, TDCIPP showed the highest estimated daily doses for all the
541 sex and age groups (Fig. 5). For adults, dermal contact was the main source of exposure, where it
542 was responsible on average for 74 % of the total calculated daily doses. Dust ingestion was
543 responsible on average for 25 % of the total daily doses. In children and toddlers, dust ingestion
544 was the major exposure pathway, where it represented on average 58 % and 67 % respectively of
545 the total daily doses followed by the dermal contact (41 % and 33 %). Inhalation showed only
546 minor contribution as most of the analytes were below LOD in the vapor phase.

547 548 **4.0. Conclusion**

549
550 This study presented for the first-time data on the concentrations, profiles, sources and health
551 exposure assessment of OPFRs considering gaseous and dust phases in the indoor and outdoor
552 environments. The inclusion of all these different samples helped us to i) highlight the similarities
553 in the observed profiles of OPFRs in the FD and outdoor dust samples and their differences from
554 the EFD samples, ii) suggest that EFD should be considered as a better representative of the indoor
555 microenvironments in similar places characterized by high concentrations of ambient particulate
556 matter, iii) highlight the importance of dermal contact as a major human exposure route for adults,
557 and thus should be considered together with the ingestion exposure route. However, toxicological

558 data expressing the effect of the exposure to OPFRs via dermal contact and inhalation are missing
559 and thus are greatly needed in future studies for between understanding of the possible overall
560 adverse health effects associated with the exposure to OPFRs from all atmospheric exposure
561 routes. In contrast to previous work, we observed strong log-linear partitioning for OPFRs between
562 gas-phase and dust samples, though offset from other brominated flame retardants. The reason for
563 the higher abundance of OPFRs in the dust relative to PDBEs and NFRs is not clear, but might
564 indicate that current physico-chemical properties of OPFRs are not well constrained.

565 **Appendix A. Supplementary data**

566 Supplementary data to this article can be found online.

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